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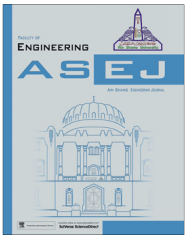

CIVIL ENGINEERING

Effect of sewage wastes on the physico-mechanical properties of cement and reinforced steel

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KEYWORDS

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Abstract The aggressive chemical attack due to salt water is one of many factors affecting the concrete deterioration. This effect includes corrosion of concrete and steel due to the exposure to the aggressive natural or artificial chemicals such as ammonia and ammonium salts. Ammonia is one of the compounds substantially in each of the remnants of sanitation plants, industrial or service of some units within building industrial waste. This work aims to study the effect of different concentrations of ammonia in the popular image on the physical, chemical and mechanical properties of different types of cement such as SRC; OPC and HSC. The electrochemical measurement (linear polarization systems) as well as infrared spectroscopy (IR) were used in this study. The behaviour of reinforced steel embedded in SRC; OPC and HSC with (5 wt.%) ammonium sulphate solution were determined. The results show that ammonia gets a harmful effect on OPC and SRC mortars but HSC shows high resistivity. Also, the reinforced steel is greatly affected in the aggressive medium containing ammonium solution.

1. Introduction

Cement, aggregates and mixing water are the principal components of concrete and reinforced concrete mixes, which are of great importance compared to the other building materials. Certain additives are added to these components depending on the area and conditions of the application to enhance the concrete strength mixes against the physical, chemical, physic-mechanical effects. The main factor for concrete to acquire a proper strength is the chain of chemical reactions between cement and mixing water. It is essential that concentration of ions in the mixing water should not exceed certain values [1].

Sulphate attack is one of the most aggressive environmental deteriorations that affect the long-term durability of concrete structures. The sulphate attack of concrete leads to expansion, cracking, and deterioration of many civil engineering structures such as piers, bridges, foundations and concrete pipes. The sulphate ions coming from the soil, ground water, and seawater, are found in combination with other ions such as calcium, sodium, magnesium and ammonium. The resistance of

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concrete to sulphate attack is determined by several factors, such as water/cement ratio, permeability, and cement characteristics, which include fineness, cement composition and associated caution type [2–10].

Calcium, sodium, magnesium, and ammonium sulphates are, in increasing order of hazard, harmful to concrete as they can cause expansion, loss of strength, and eventually transform the material into a mushy mass [11].

The sulphate attack is generally attributed to the reaction of sulphate ions with calcium hydroxide and calcium aluminates hydrate to form gypsum and ettringite. Gypsum and ettringite are formed as a result of sulphate attack are significantly more voluminous (1.2–2.2 times) than the initial reactants [11,12]. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. The concrete deterioration by the effect of ammonium sulphate is the most aggressive concrete corrosion. The concrete corrosion takes place according to the following mechanism:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \text{ (Gypsum)} + NH_3 \uparrow \text{ (Gas)}$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 \cdot 2H_2O + 24H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \text{ (Ettringite)}$$

Only expansive gypsum is formed and no protective layer like brucite is created. This not only leads to expansion due to the formation of gypsum and ettringite $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ but also to intensive dissolution of cement hydrates [13]. Another contributory mechanism is likely to be the formation of ammonia gas, which readily diffuses from the concrete enabling the gypsum formation reaction to eventually proceed to completion rather than to establish equilibrium. Diffusion of ammonia gas from the concrete will also render the concrete more porous and permeable and thus more susceptible to further attack from ammonium sulphate solution [14,15].

There are little available data concerning ammonium sulphate attack; however, some of which indicates that this salt is very harmful to concrete [16–18]. The role of admixtures such as silica fume, fly ash, or blast furnace slag on the improvement in the ammonium sulphate resistance of concrete has not yet been clearly established; some researchers report a negative effect [13], while others claim their effectiveness [16]. In a previous study, Péra et al. [18] have shown that silica fume was more efficient than metakaolin with regard to the resistance of concrete to ammonium sulphate, at a level of 10% Portland cement replacement. Nevertheless, some swelling occurred and the mass loss was important (10–15%).

EN 206-1: 2000 [19] indicate that, a level of NH_4^+ of 15–30 mg/l should be regarded as slightly aggressive weight loss, 30–60 mg/l as moderately aggressive, and greater than 60 mg/l highly aggressive. Ammonium compounds are found to occur in sewage, typically 30 mg NH_4^+/l; certain industrial waste water and sludge treatment processes will have concentrations up to 500 mg NH_4^+/l.

2. Experimental techniques

The materials used in this investigation were ordinary Portland cement (OPC), sulphate resisting cement (SRC) and high slag cement (HSC) provided from Egypt Cement Company. Also ammonium sulphate solution 5% was used as aggressive medium. The surface area of SRC, OPC and HSC were 3150, 3061 and 3528 cm^2/g respectively. The chemical composition of these cements is listed in Table 1. Each dry mix was homogenized in a porcelain ball mill with two balls for 1 h using a mechanical roller to assure complete homogeneity. The pastes and mortars were mixed with the required water of standard consistency. The compressive strength was measured on cement mortars according to ASTM method using 50 mm cubic moulds [8]. The cement mortars were cured in a humidity chamber at 23 ± 1 °C for 24 h, and then demolded and cured under tap water for 28 days, then immersed in 5% ammonium sulphate solution up to 1 year. The hydration behaviour of each mix was followed by determination of free lime, total porosity and bulk density. The aggressive attack was determined through the measurements of compressive strength at different time intervals up to 1 year.

2.1. The electrochemical measurement

The electrochemical behaviours of reinforced steel are determined by linear polarization techniques. The working electrode was made in the form of rod with cross sectional areas of 1 cm^2. The rod was coated by epoxy resin leaving only the base cross sectional area then fixed in a tube with an appropriate diameter by cement mortar to face the test solution. Before each experiment the exposed area of the electrode was mechanically polished with successively different grades of metallurgical emery paper starting from 400° to 1200°, until it's surface becomes free from scratches and other apparent defects. It was then rinsed with distilled water and dried in air. Analytical grade chemicals and distilled water were used for preparation of 5% ammonium sulphate solution. The electrochemical measurements are determined by Volta-lab 40 PGZ100 "All-in-one" Potentio-state/Galvano-state system (made in France).

2.2. Infrared IR spectroscopy

Infrared (IR) light is electromagnetic radiation with a wavelength longer than that of visible light, measured from the nominal edge of visible red light at 0.74 micrometres (μm), and extending conventionally to 300 μm. These wavelengths correspond to a frequency range of approximately 1–400 THz and in-

Table 1 Chemical composition of the starting materials.

Chemical composition ((%)	OPC	SRC	SC
CaO	64.80	50.90	40.30
SiO_2	21.40	25.6	35.50
Al_2O_3	6.36	3.97	5.40
Fe_2O_3	3.35	4.95	8.89
MgO	1.85	2.10	2.98
SO_3	1.77	1.94	0.11
K_2O	0.54	0.11	0.32
Na_2O	0.28	0.13	1.25
TiO_2	0.02	0.01	0.01
LOI	0.81	0.94	1.38
C_3S	48.38	40.54	45.33
C_2S	24.15	42.65	36.44
C_3A	11.18	5.14	4.87
C_4AF	10.19	8.17	11.24

clude most of the thermal radiation emitted by objects near room temperature. Microscopically, IR light is typically emitted or absorbed by molecules when they change their rotational-vibration movements. The infrared spectrophotometer model Perken Elmar lumbedo 2 was used to confirm the presence of lime at 3600 cm^{-1} and ammonium sulphate at 1016 cm^{-1}.

3. Results and discussion

3.1. Physical properties

The variation of the bulk density of the investigated mixes is represented in Fig. 1. It is clear that, the bulk density increases up to 3 months in OPC and 6 months in both high slag and SRC, respectively. This behaviour is mainly related to the increase of hydration products which precipitate within the pores originally filled with water. The reduction of bulk density in all types of cement may be due to the dissolution of cementenus matrix. The variations of total porosity of the investigated mixes are graphically represented in Fig. 2. The results of total porosity for all hardened specimens are typically correlated with the results of bulk density, where the total porosity inversely proportional to bulk density.

3.2. Chemical properties

The variation of free lime content with curing time of hardened cements is shown in Fig. 3. The free lime of plain cement increases up to 3 months then decreases up to 1 year. This is mainly related to the high liberation of calcium hydroxide $Ca(OH)_2$, then the free lime content decreases with time and the rate of its consumption increases to produce gypsum. In presence of high slag cement, the free lime decreases in all interval time due to the pozzolanic reaction of slag portion with the free lime to produce CSH. But this reaction decreases the pH values due to the formation of weak alkali which decreases the stability of CSH. This variation is very important in the formation passive layer and for the mechanical properties of cement mortar. This process is reduced sharply in presence of high slag cement (HSC).

3.3. Infrared spectroscopy (IR)

The variation of Infrared spectroscopy (IR) in HSC, SRC and OPC cements is represented in Fig. 4. The variation in the band at 3600 cm^{-1} is limited and changed according to the free lime content. The variation in the band at 1480 cm^{-1} is mainly related to the carbonation, which is sharply reduces with time. The effect of ammonium sulphate is explained at 1016 cm^{-1}, which produces the reduction in the formation of CSH due to the sulphate attack and the reduction in pH .

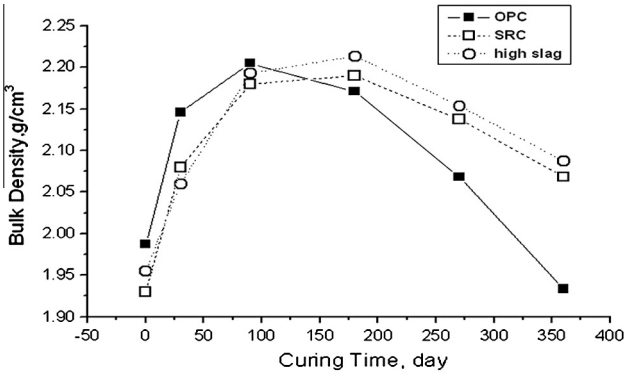

Figure 1 Bulk density (g/cm^3) of hydrated OPC, SRC and high slag cement immersed in ammonium sulphate (5%) up to 1 year.

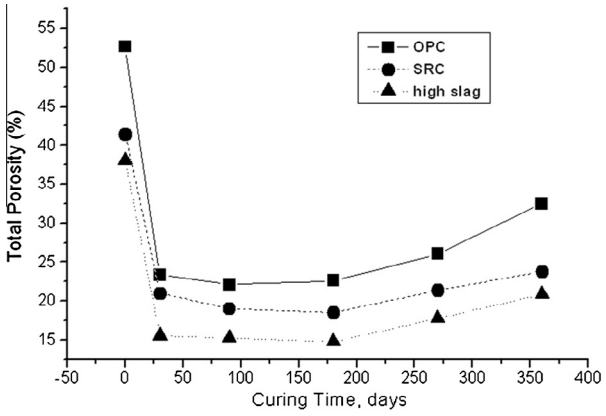

Figure 2 Total porosity (%) of hydrated OPC, SRC and high slag cement immersed in ammonium sulphate (5%) up to 1 year.

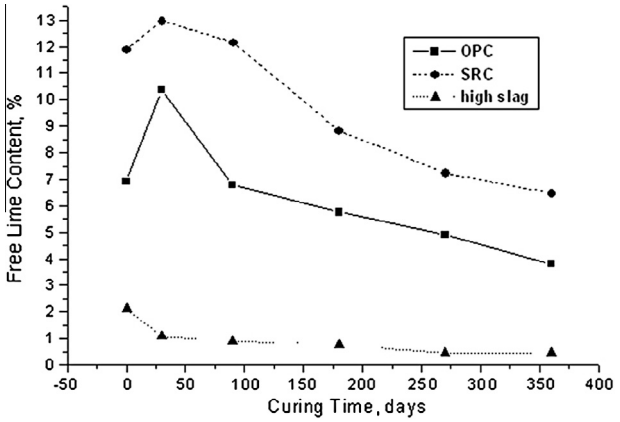

Figure 3 Free lime (%) of hydrated OPC, SRC and high slag cement immersed in ammonium sulphate (5%) up to 1 year.

3.4. Mechanical properties

The variations of compressive strength values of different cement mortars immersed in 5% ammonium sulphate solution with curing time up to 1 year are graphically represented in Fig. 5. The results show that the compressive strength increases for plain cement up to 3 months, then decreases with time. SRC shows the best results comparing with OPC, which deteriorates rapidly. This behaviour is mainly related to the variation of C_3A percentage which reacts with gypsum to produce ettringite.

In high slag cement, the compressive strength increases up to 6 months due to the formation of binding materials which result from the pozzolanic reaction. The variation of compressive strength is pointing to the high resistivity of slag cement which mainly related to the low C_3A content and the consumption of free lime.

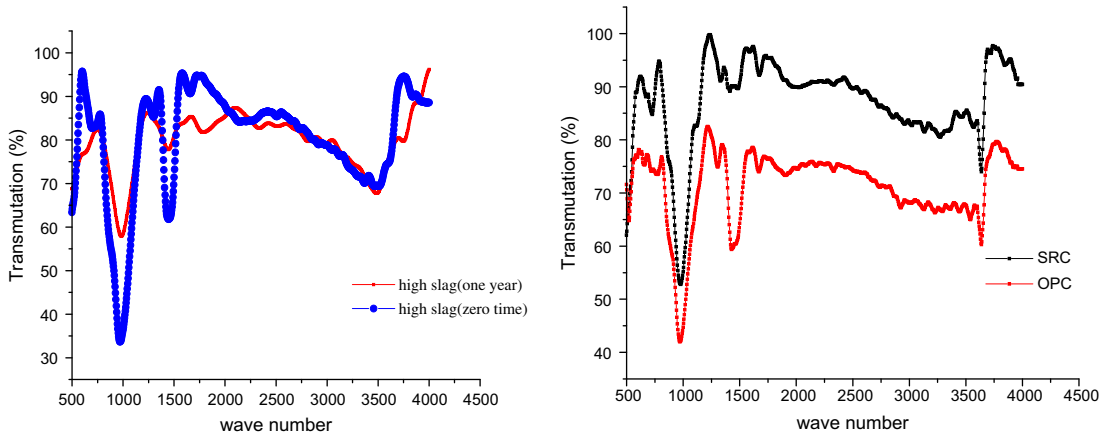

Figure 4 IR spectroscopy of hydrated high slag cement, SRC and OPC immersed in ammonium sulphate (5%) up to 1 year.

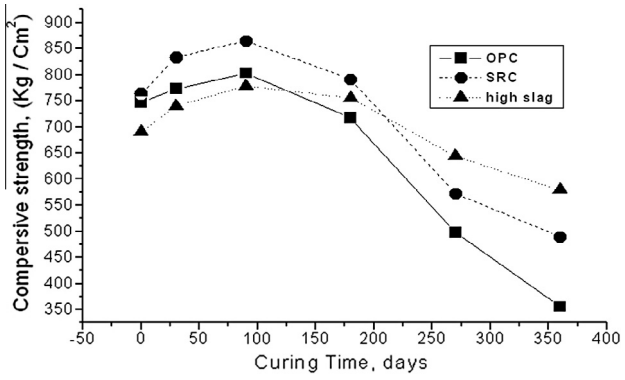

Figure 5 Change in compressive strength of hydrated OPC, SRC and high slag cement immersed in ammonium sulphate (5%) up to 1 year.

3.5. Linear polarization

The electrochemical behaviour of reinforced steel imbedded in different types of cement mortars which immersed in ammonium sulphate solution was determined and graphically represented in Fig. 6 as Tafel plot diagram. The Tafel plot of reinforced steel impeded in OPC mortar shows that the free corrosion potential is shifted to more positive value in most time intervals. This increases are mainly related to the liberation of calcium hydroxide $Ca(OH)_2$, which produces during the hydration process. From the variation in Tafel plot, the passivation process is controlled by cathodic reaction in most intervals. The variation in I_{corr} increases with time, due to deterioration of cement and sulphate attack on the passive layer. The polarization resistance gets the opposite trend comparing with corrosion current. This behaviour is mainly due to distortion of passive layer on the surface of reinforced steel.

Fig. 7 represents the variation in Tafel plot of reinforced steel included in SRC mortar. The free potential, is shifted to more positive. This is mainly due to the variation of free lime in cement species, which decreases with time, due to the formation of gypsum. Also, corrosion current is decreased, due to the formation of passive layer and cement physical protections. But, the corrosion current density is increased at the end of determination, due to the sulphate attack. The polarization resistance gets the opposite direction as shown in OPC.

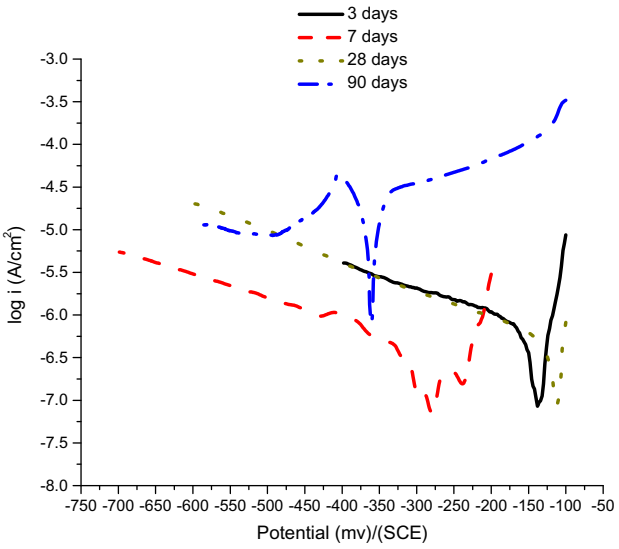

Figure 6 Tafel plot of reinforcing steel included in OPC immersed in (5%) ammonium sulphate solution.

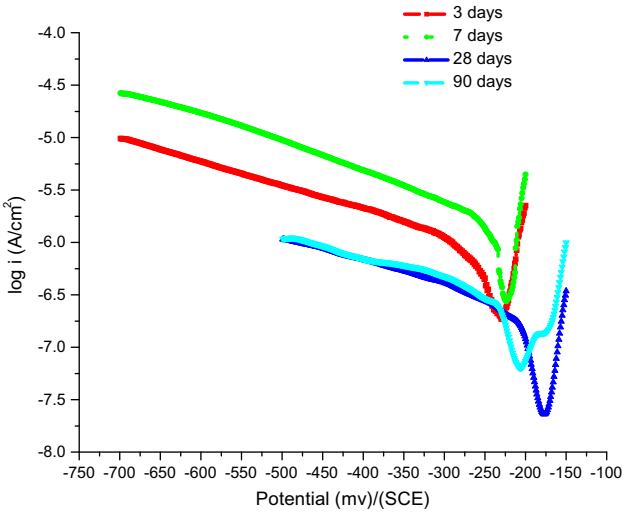

Figure 7 Tafel plot of reinforcing steel included in SRC immersed in (5%) ammonium sulphate solution.

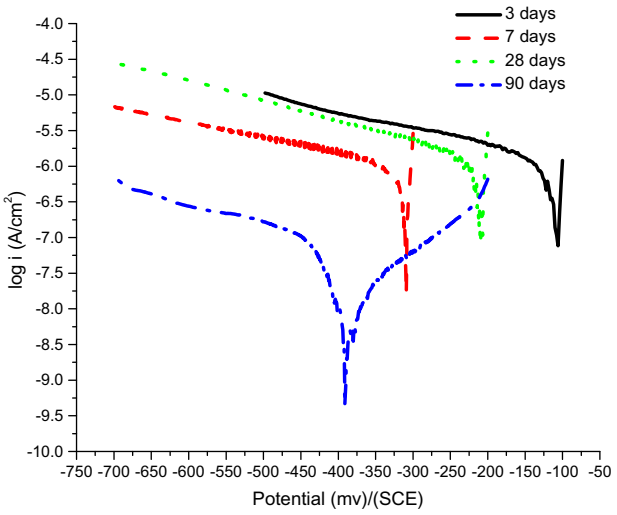

Figure 8 Tafel plot of reinforcing steel included in high slag cement immersed in (5%) ammonium sulphate solution.

Fig. 8 indicates the variation of the electrochemical behaviour of reinforced steel holed in high slag mortar, the free potential, shifted in most intervals to the negative values. This variation is increased at later ages. The corrosion current density is decreased with time due to the physical protection in presence of pozzolanic reactions and chemical passivation. These results show the high resistivity of cement to sulphate attacks. Also this variation is commented the probability of high slag to protect steel in high aggressive medium containing ammonium sulphate solution.

4. Conclusions

In this paper a serious of experiments was performed to investigate the effect of different concentrations of ammonia on the physical, chemical and mechanical properties of different types of cements. The behaviour of reinforced steel embedded in SRC; OPC and HSC mortars with 5% ammonium sulphate solution were measured. Based on the experimental results presented in this paper, the main conclusions are as follows:

1. OPC and SRC mortars gets a harmful effect in the aggressive medium containing ammonium sulphate.
2. Solution but HSC shows high resistivity to sulphate ammonium attack.
3. Slag cement must be used in reinforced concrete buildings subjected to ammonia instead of OPC and SRC.
4. The reinforced steel is greatly affected by the presence of ammonia and aggressive ammonium ions.
5. Maintenance and treatment must be measured according to the electrochemical methods.

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